Dynamic piezoelectric response of relaxor single crystal under electrically driven inter-ferroelectric phase transformations

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Abstract

In this work, we demonstrate that xPb($In_{1/2}Nb_{1/2}$)O_3-(1-x-y)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$y$$PbTiO_3$ [110]-poled domain-engineered relaxor single crystals can be dynamically and reversibly driven through a ferroelectric-ferroelectric phase transition exhibiting highly enhanced piezoelectric response in a wide range of frequencies. Realization of this phase switching requires an applied compressive stress close to the critical values for the inter-ferroelectric phase transition, which can then be induced by a relatively small electric field ($\leq$ 0.2 kV/mm). The required critical stress was established by *in situ* stress and X-ray diffraction measurements. The effective d_{32} coefficient measured dynamically up to 70 Hz was shown to be consistently twice that of the linear piezoelectric mode measured below the phase transformation region. The crystal was installed into a prototype transducer based on a Tonpilz configuration. The performance of the transducer was tested in water and showed up to 15 dB_{SPL} higher acoustic power radiated when the crystal was driven through the phase transition than when operating in the linear piezoelectric regime.

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Continued development of highly efficient transducers for high-power, low-frequency, compact-sized sound projectors demands a new class of materials with enhanced properties. High power underwater acoustic projectors are generally very large and heavy, but recent single crystal transducer development [1,2] promises significant size and weight reductions [3,4]. Specifically, domain-engineered relaxor $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3}O_3\text{–}xPbTiO_3$ (PMN-PT) and $(1\text{–}x)Pb\,Zn_{1/3}Nb_{2/3}O_3\text{–}xPbTiO_3$ (PZN-PT) systems poled along the equivalent nonpolar $(001)_C$ pseudocubic direction are of highest interest. The crystals with compositions close to the morphotropic phase boundary (MPB) [5–9] showed high electromechanical coupling factors ~ 0.9, and large piezoelectric coefficients up to 2000 pm/V [3-5]. It was concluded that this phenomenon of enhanced piezoelectricity can be linked to the presence of intermediate monoclinic (F_M) and orthorhombic (F_O) ferroelectric states in between the ferroelectric rhombohedral (F_R) and tetragonal (F_T) phases, allowing for enhanced polarization rotation [3-8]. This F_R-to-F_T phase transformation can also be accessed electrically [3] with maximum strains on the order of 1% [4] in binary compositions of PZN-PT, whereas large anhysteretic strains of up to 0.6% in PMN-PT [5] have been reported. Electrically induced discontinuities in strain were studied by Davis *et al.* [11] and were asserted to be a first-order-like phase transition.

In addition, an elastic instability was reported in both binary and ternary domain engineered single crystals subjected to uniaxial stresses [9–12]. The isothermal elastic response with harmonic stress (~50 MPa) of domain engineered (3-3 and 3-2 modes) PZN-PT single crystals with composition near MPB was investigated by Amin and Cross [13]. Okawara and Amin [11] observed a reversible and hysteretic stress-strain response of these crystals that is characterized by a large and sharp strain discontinuity (up to 0.5%) occurring at a critical stress. This strain was attributed to a stress-induced F_R to F_O transition caused by polarization rotation under mechanical

compression. The reversible effect is speculated to be due to internal electric fields such as those associated with charged domain walls [12]. Similar observations in domain engineered ternary xPb($In_{1/2}Nb_{1/2}$)O_3-(1-x-y)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$y$$PbTiO_3$ (x=0.24, y=0.32) (PIN-PMN-PT) single crystals were reported by Finkel *et al.* [14]. Recently, using mechanically biased PIN-PMN-PT (110) poled crystals we presented a method to deliver strain levels of ~0.5% at relatively low (~ 0.1 kV/mm) drive fields, representing a fourfold increase in strain at only 20% of the drive field as compared to those of other piezoelectric relaxor ferroelectric single crystals (*e.g.* PMN-PT) [15,16]. Despite the critical importance for applications these phase switching phenomena in PIN-PMN-PT crystals were reported predominately under quasi-static or nearly DC conditions. So far there has been limited work extending this intrinsic structural phase switching phenomenon into higher frequency range required for real sound generating devices. Further progress in exploiting these large enhanced piezoelectric properties potentially leading to transducers with even greater performance requires the study of the underlying mechanism of this phase transformation. In this work, we demonstrate dynamic response based on the large electro-strain generated in the crystalline phase transition found in relaxor ferroelectric [110]-oriented, domain-engineered PIN-PMN-PT single crystals. To achieve this, we have applied a compressive mechanical stress close to the critical compressive stress σ_c needed for phase transformation from F_R to F_O, *i.e.* mechanical confinement. Compared to the field-induced strain of ~0.5 % at 2 kV/mm in PZN-PT single crystals as reported by Park *et al.* [7], the present results show similar strains but with over an order of magnitude reduction in field.

Rectangular bars of PIN-PMN-PT with dimensions of 4 × 4 × 12 mm were procured with the longest edge oriented along the [001] while the other faces were oriented along the <110>.

These bars were compressed along the [001] in several different loading devices for testing of the piezoelectric coefficient d_{32} at different frequencies and compressive stresses.

First in order to confirm if the prestress is sufficient for reaching the required critical threshold needed for realization of the transition to a phase that had been previously described as orthorhombic [8, 10, 11, 13-15]. To ensure we can achieve this F_R-to-Fo phase transformation we recorded the stress- strain response this time using a custom-built stress rig permitting *in situ* X-ray diffraction characterization (see Supplementary information*[1]). Full 3D reciprocal mapping with a 2D camera revealed the structural phases present as a function of stress and field (more details can be found in ref. [18]). Strain was measured with a strain gauge affixed to the sample on the $(\bar{1}10)$ specular face, aligned in the [001] direction. Figure 1 shows the X-ray diffraction $(\bar{1}10)$ – referenced here with pseudo-cubic indices - lattice parameter change as a function of applied uniaxial compressive stress at zero applied electric field along with simultaneously measured strain, corrected with a Poisson ratio of 0.37 to make the two graphs match. An initial quasi-linear strain softening is identified as the low stress F_R phase. At a critical stress, $\sigma_c > 20$ MPa the elastic properties changed dramatically to a much stiffer response, characteristic of the high-stress phase F_O . The X-ray diffraction data from the (111) reflection plotted as X-ray intensity (H-K) contour plots at constant L (L=1.131) (Figure 1, insets) show two distinct (HKL) diffracting conditions at low stress transforming to only one (HKL) condition at stresses above σ_c.

Next, the quasi-static (< 1 Hz) stress-strain behavior of the crystals was characterized in a load frame (Instron), and from this measurement the critical stress σ_c for the phase transition was determined to be close to the values evaluated from the *in situ* X-ray experiment and to the values

*[1] The data that supports the findings of this study are available within the article and its supplementary material.

reported earlier [17] . Strain and polarization hysteresis curves were measured with a ferroelectric test system (Radiant Technologies) while the sample remained mechanically confined under stress along the [001] direction (as shown in the insert of Figure 1a) accompanied by an electric field applied along [110]. Several of the resulting strain vs. electric field curves at variable compressive stress ranging from 20 to 26 MPa are shown in Figure 2. It should be noted that in this range of compressive stress, an amplitude of the applied electric field < 0.2 kV/mm was sufficiently high to cycle from F_R to F_O and back to F_R. This sharp jump in strain (up to 2000 microstrain) was triggered reversibly with low hysteresis and approximately independent of pre-stress conditions.

Subsequent to this, a dynamic piezo-analyzer was used to evaluate the direct d_{32} piezoelectric response under mechanical compressive load up to 50 MPa, but this time with an AC stress signal (at 1 Hz and 70 Hz) applied superposed on the static preload value for three preloads representing F_R (< 20 MPa) , F_{TRANS} (~ 23 MPa) and F_O (>26 MPa) phases . The dynamic charge-stress relation was measured with a home-built press. The press contains a quartz reference sensor to measure the force, a PZT actuator, two stiff zirconia columns with steel caps for electrical contacts between which the sample is placed, and a stepper motor, all connected mechanically in series and contained within a rigid steel frame. The AC stress is generated by the PZT actuator. The piezoelectric charges produced by the quartz sensor and the sample are measured by two separate charge amplifiers and recorded by an oscilloscope. Both longitudinal and transverse piezoelectric response can be measured by appropriate orientation of the electroded faces with respect to the crystallographic axes of the sample and direction along which the stress is applied. For charge induced by stress during the phase transition, the compressive force was only applied from 0 to 40 MPa by the stepper motor. The total duration of force application and release for this technique lasts approximately 2 minutes. More details can be found in Refs. [19,20].

The stress-polarization dependence is plotted in Figure 3(a). It is notable that there is almost no observable hysteresis upon loading and unloading. There are three clearly observable regions with different slopes (as denoted by blue, red and green symbols in Fig 3(a)) which correspond to the two phases separated by the sharply increasing polarization region where the transition between them is occurring. As shown by d_{32} versus stress in the inset of Figure 3(a), the value is relatively constant in the F_R condition with a large spike at stresses near the phase transition at ~20 MPa that corresponds to the optimal loading condition (σ_c) for F_{TRANS}. At higher stress values, d_{32} drops off significantly once the crystal is in the orthorhombic regime.

The crystals were also tested in a special spring and mechanical screw loaded fixture and compressively stressed in the ranges as described above. At these loads, bipolar electrical field-strain hysteresis measurements were performed at fields of 0.3 kV/mm at 10 Hz in order to characterize the converse d_{32}^* piezoelectric coefficient (*i.e.* normalized maximum strain at the maximum applied electric field). The electric field dependence of the strain is plotted in Figure 3(b) while the crystal is held at a pre-stress corresponding to either the F_R or F_O phases or at σ_c to achieve the phase transition (F_{TRANS}). There is a clear difference in the total strain generated for the same electric field swept at 10 Hz.

The d_{32} and d_{32}^* values as calculated from the slopes of these experiments , as well as the values calculated from the dynamic d_{32} setup , are summarized in Table 1 for the three loading conditions of interest corresponding to F_R , F_O and F_{TRANS} regions as denoted by blue , red and green symbols in Fig 1a) From the data in Table 1 it is clear that the d_{32} and d_{32}^* values are substantially higher in the transition region, although there is a fairly large variation in magnitude depending on the measurement technique. The differences may be due to how the measurements

were done (i.e. changes in the boundary conditions in different load frames) since the dynamic d_{32} measurement showed only a modest decrease as the frequency changed from 1 to 70 Hz.

After initial characterization of the crystal under low frequency drive conditions the crystal was installed into a transducer assembly (a Tonpilz-type design) driven over broader range of frequencies in tens of kHz range. For this, electrical leads were attached to the electrodes on the surface of the crystal, and the crystal was inserted into the transducer apparatus as shown in the schematic in Figure 4. A screw on the top was used to apply an adjustable compressive pre-load to the crystal. The crystal was placed between two ceramic shims, and for optimal boundary conditions there were several spring washers below the head adapter. The sound was transmitted from the cone on the opposite side, which was submerged in water and directed at the hydrophone. The transducer was not potted with oil or otherwise waterproofed and remained above the surface of the water during testing. Initial testing with a square wave pulse was done at the Naval Undersea Warfare Center in Newport, RI. Comparison tests, and then subsequently final characterization discussed herein, were performed at the NRL facility described in details in Supplementary section[2].

There are various resonances within the structure and those resonances shift in frequency and amplitude with applied stress due to the change in sample properties as confirmed by impedance measurements (Fig. 5(a)); however the general trend in the sound pressure level (SPL) data is in agreement with the measured piezoelectric coefficients for the three different pre-stress conditions. The SPL for a 400 V chirp pulse with broad spectrum waveform [Figure 5(b)] shows an overall higher result for the crystal under F_{TRANS} loading conditions in the entire frequency range, and particularly above 10 kHz. At a local maximum near 27 kHz, there is an enhancement

[2] The data that supports the findings of this study are available within the article and its supplementary material

of 15 dB in SPL between the F_{TRANS} (76 dB) and F_R (60 dB) data and a similarly large enhancement as compared to when the sample is in the F_O regime. This suggests that even at much higher frequencies than shown in Table 1, the relationship between the d_{32}^* coefficients still holds and that the corresponding increase in strain generated through the phase transition directly translates to an increase in acoustic pressure level.

We also monitored temperature of the crystal inside the transducer using an IR camera (FLIR E95) while driving at 500 V at 1000 Hz through the phase transition for ~ 30 min to achieve equilibrium and found that the sample heating is much less than 1 ºC under continuous operation. With negligible heat dissipated and the lack of fatigue previously observed for tens of millions cycles in these PIN-PMN-PT [14-16], we believe these results demonstrate the great potential for using this phase transformational regime for high-power sound-generation transduction. With further chemical and microstructural optimization of single crystal materials - specifically focused on their dynamic piezoelectric properties under stress - we anticipate that such large strains can be generated at even lower fields .

In summary, we investigated and demonstrated broadband dynamic nonlinear piezoelectric response in [011] poled ferroelectric 0.24PIN-0.44PMN-0.32PT relaxor single crystals and how to capture this large response for potential application in acoustic transducers. It was shown that as compared to linear rhombohedral or orthorhombic modes, the effective nonlinear dynamic d_{32} or d_{32}^* coefficient is almost a factor of two higher, and this enhancement persists over a wide range of frequencies. Through the use of *in situ* compressive-stress X-ray diffraction the optimum mechanical bias was identified as being close to the critical stress for triggering rhombohedral – orthorhombic phase transformations, and we demonstrated excellent performance of a prototype transducer element and the viability of exploiting this effect. The sound pressure level was

enhanced (10-15 dB) throughout a large frequency range when the crystal is driven through the phase transition as compared to when it was in either of the linear piezoelectric regimes. The advantage of implementing nonlinear phase switching that is permitted in [110]-poled PIN-PMN-PT single crystals leads to opportunities to produce acoustic sources with enhanced performance at lower applied fields for highly efficient sound transduction.

Supplementary Material

The supplemental material contains full description of a custom-built stress rig permitting *in situ* X-ray diffraction characterization and also detailed apparatus and the system for in water SPL tests for acoustic sensor.

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All data generated or analyzed during this study are included in this published article (and its supplementary information files) and also are available from the corresponding author on reasonable request.

Table 1: Values of d_{32}^* and d_{32} derived from bipolar electric field – strain hysteresis (10 Hz, a – E-S Hyst.), slopes of stress-polarization (20 mHz, b.), and from dynamic d_{32} measurements (1 and 70 Hz, c.).

	F_R	F_{TRANS}	F_O	*Setup*
20 mHz	1690 pC/N	3440 pC/N	184 pC/N	b
1 Hz	1200 pC/N	1700 pC/N	222 pC/N	c
10 Hz	824 pm/V	2090 pm/V	98.0 pm/V	a
70 Hz	1310 pC/N	1570 pC/N	209 pC/N	c

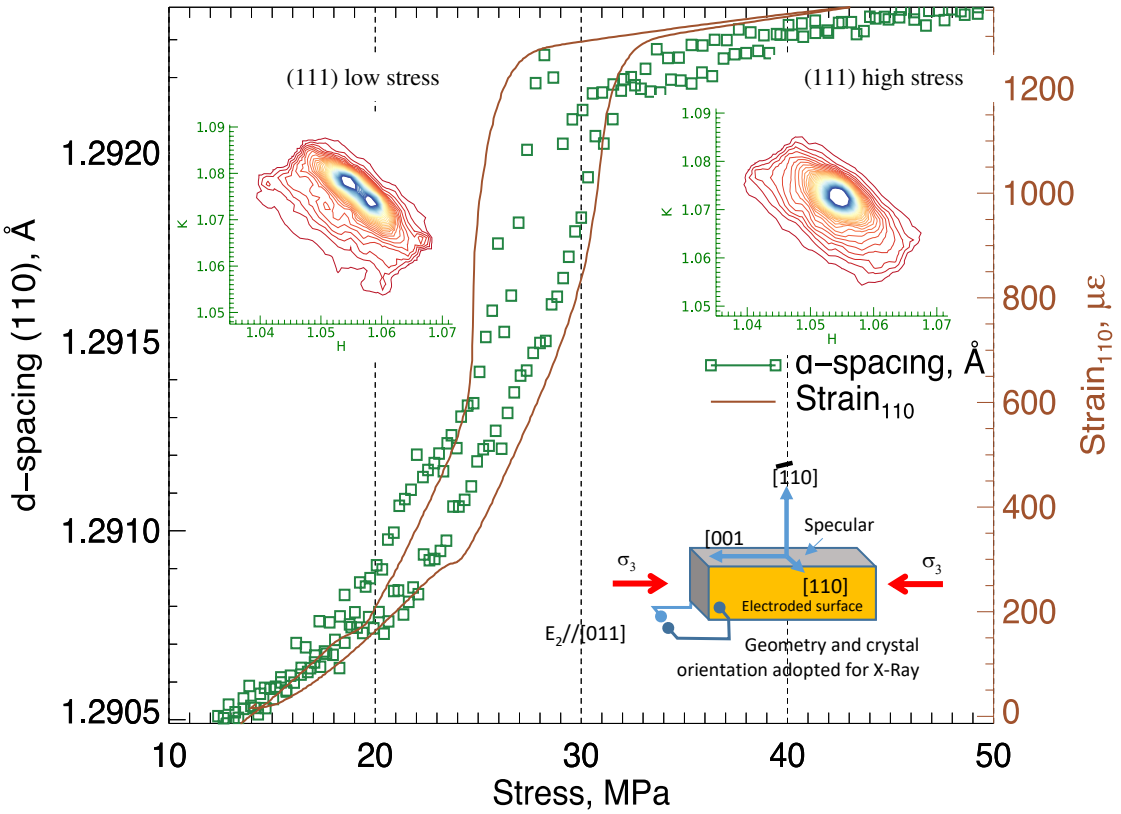


Figure 1. *In situ* X-ray diffraction of the ($\bar{1}$10)c reflection (d-spacing - green squares, and all reflection indices based on a pseudo cubic unit cell) compared to macroscopic strain (solid line) measured as a function of applied uniaxial stress at zero applied field. There is a stress-induced transformation from two phases/domains at low stress to one single (higher modulus) phase at high stresses. The features present in the diffraction data are real and repeatable and indicate pathways from low stress rhombohedral symmetry to a higher stress lower symmetry phase. Contour maps show the (111)*c* diffraction contrast for low stress (10 MPa), and highest stress states (48 MPa), and the sample X-ray configuration schematic is provided for orientation clarity. Macroscopic strain is recorded along (001)c and a Poisson ratio of 0.37 is used to match to the X-ray data.

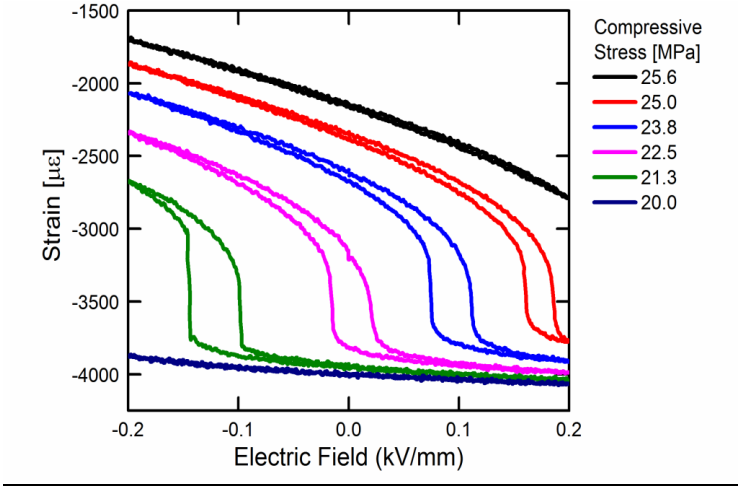
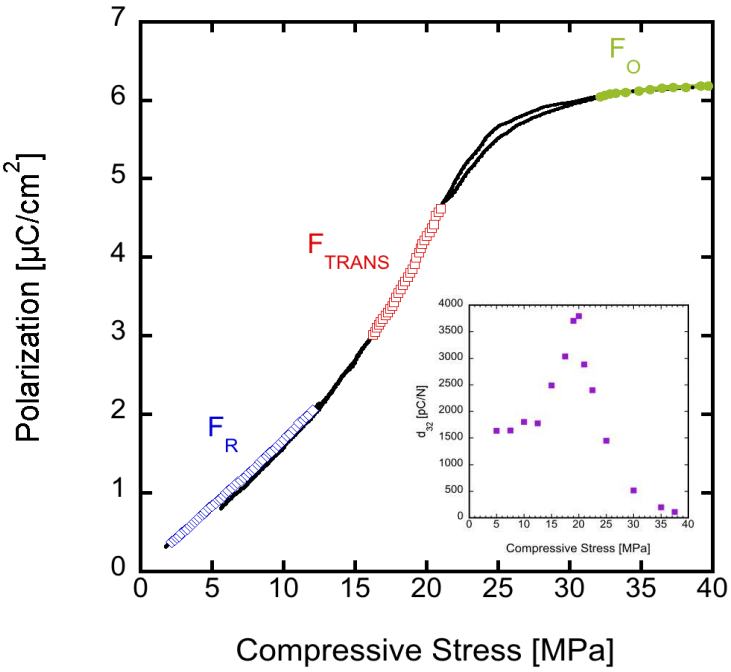


Figure 2 Strain measured quasi-statically at 1 Hz depicting large nonlinearity due to the F_R to Fo phase transition at various stresses from 20-26 MPa.



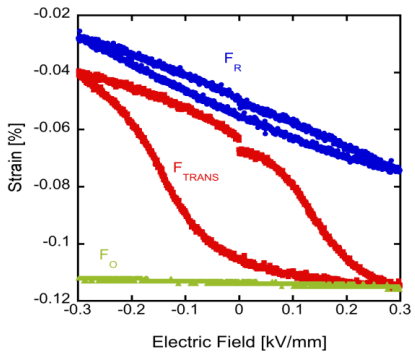


Figure 3. (a) Stress dependence of the polarization at 20 mHz with slopes used for d_{32} highlighted at the three regions of interest F_R, F_{TRANS}, and F_O denoted by blue, red and green symbols respectfully that was also used to calculate the slope for d_{32} values reported in the Table 1. Inset shows d_{32} vs. stress as calculated from the slope. (b) Strain as a function of electric field measured at 10 Hz for three corresponding regions (F_R, F_{TRANS}, and Fo) as above.

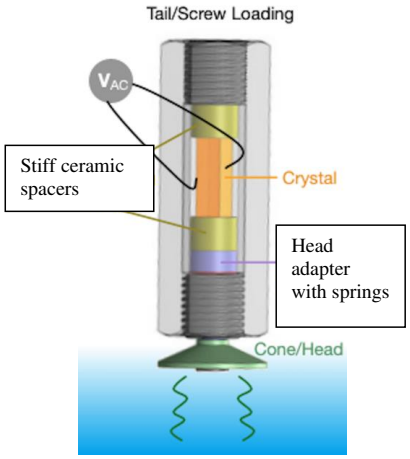
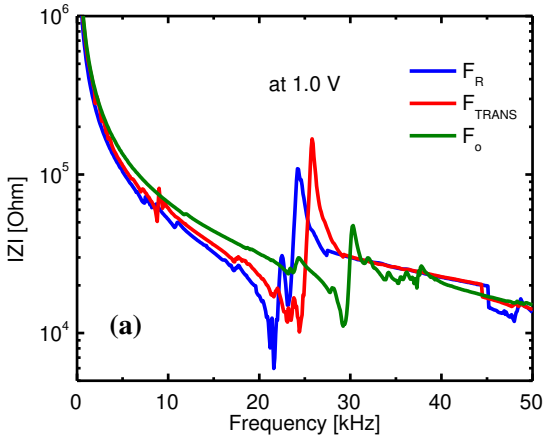


Figure 4: Schematic of transducer used in the SPL in-water measurements, explaining crystal placement and application of mechanical bias.



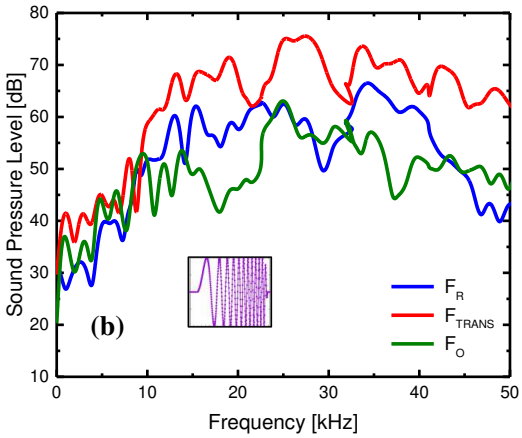


Figure 5. (a) Impedance as a function of frequency at 1 V drive**.** (b) Sound pressure level for three regimes (F_R, F_{TRANS}, and F_O) in water at 500V drive , normalized to 1m. The inset shows the formed 1- 40 kHz pulse used for excitation.

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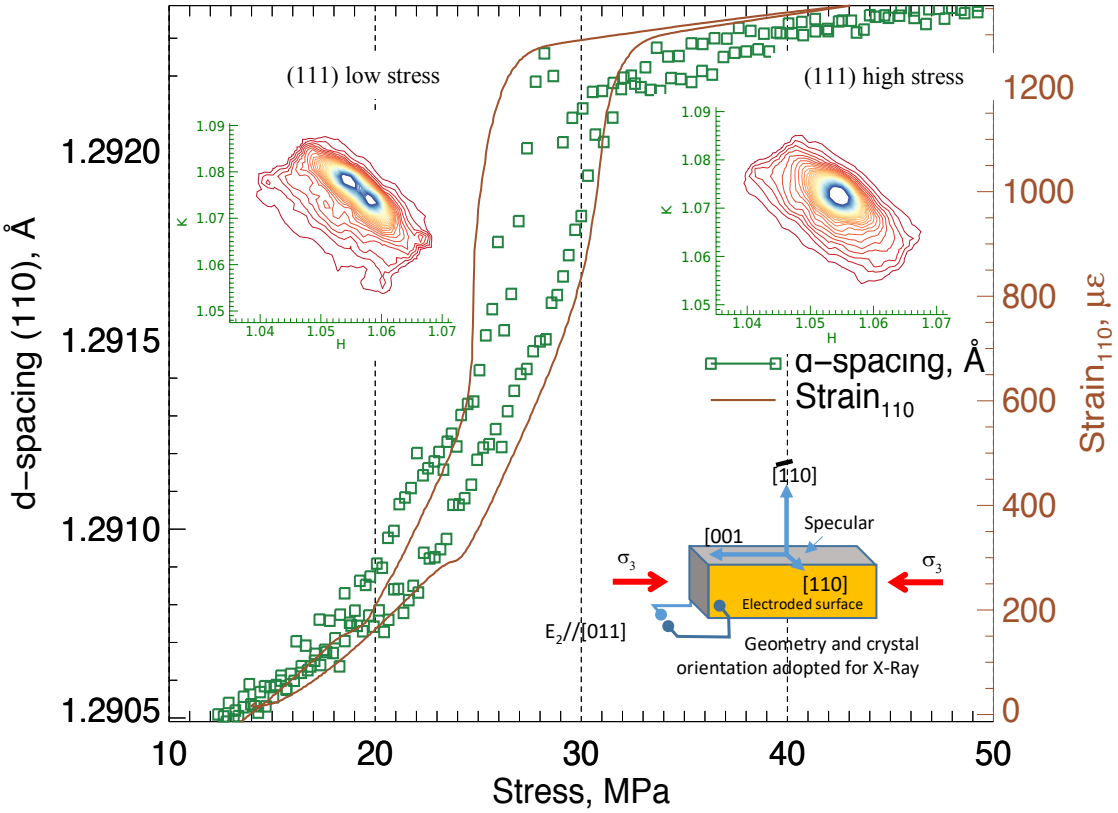

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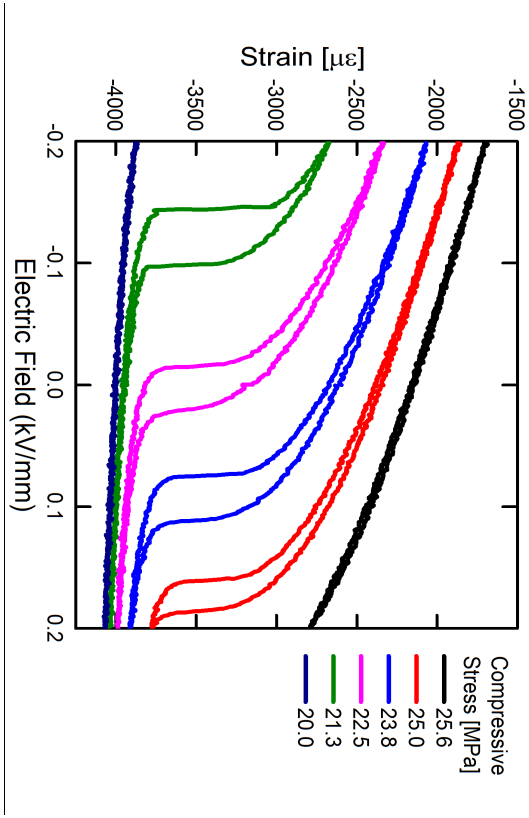
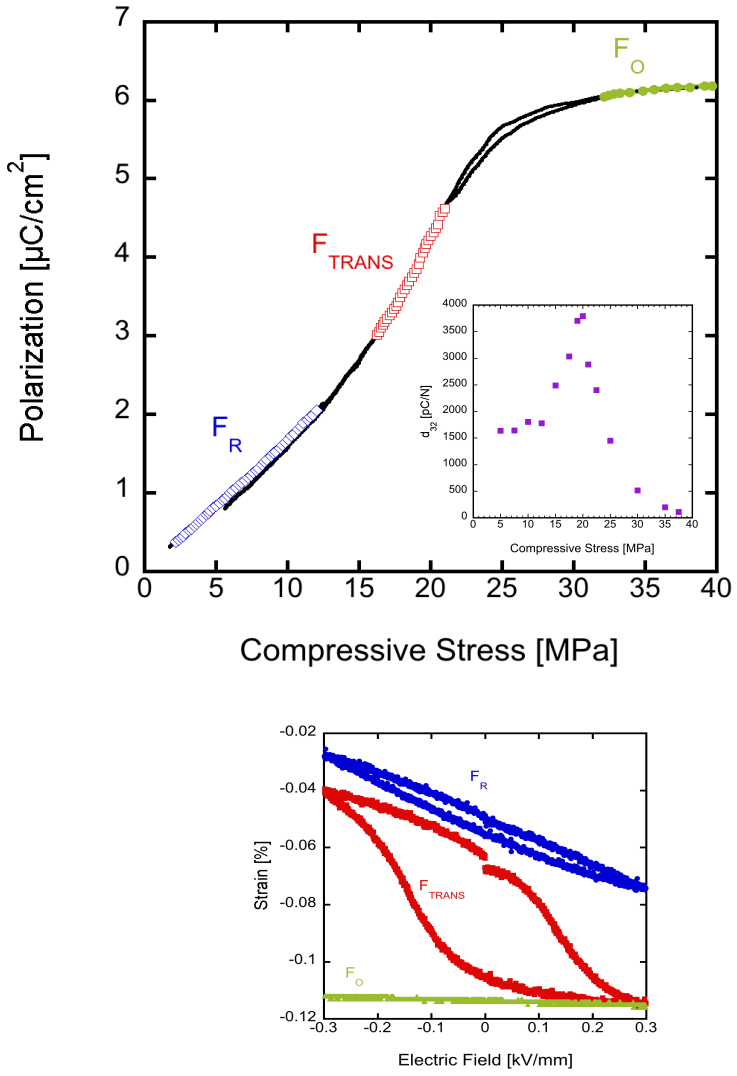


Figure 2



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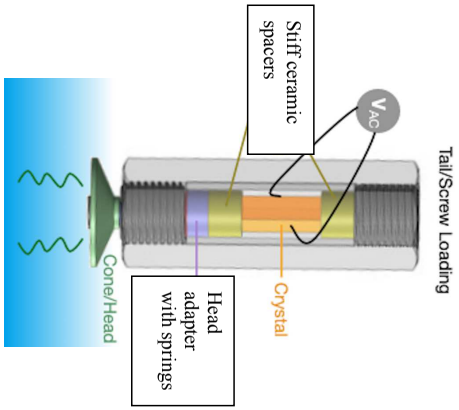
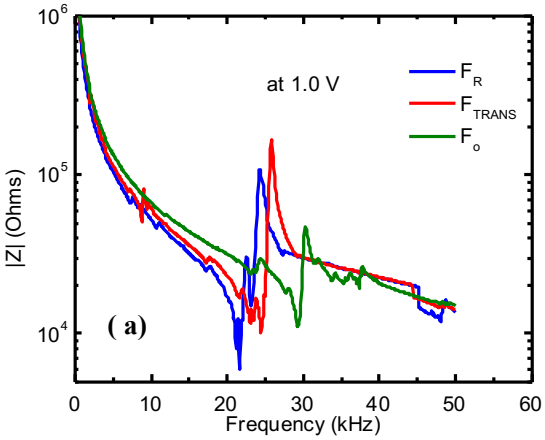


Figure 4:



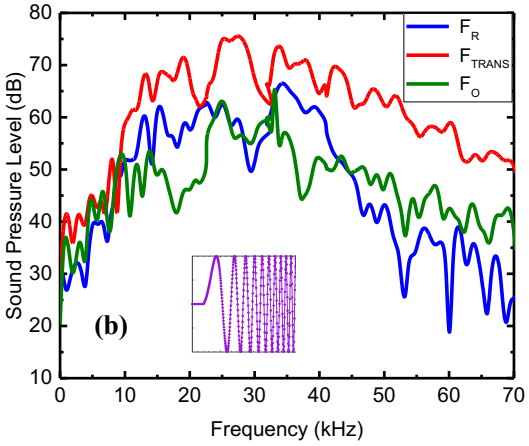


Figure 5.